

REMARKS

This Preliminary Amendment cancels, without prejudice, claims 1 to 5 in the underlying PCT Application and adds new claims 6 to 10. The new claims, inter alia, conform the claims to U.S. Patent and Trademark Office rules and do not add new matter to the application.

In accordance with 37 C.F.R. § 1.121(b)(3), the Substitute Specification (including the Abstract, but without the claims) contains no new matter. The amendments reflected in the Substitute Specification (including Abstract) are to conform the Specification and Abstract to U.S. Patent and Trademark Office rules or to correct informalities. As required by 37 C.F.R. §§ 1.121(b)(3)(iii) and 1.125(b)(2), a Marked-Up Version of the Substitute Specification comparing the Specification of record and the Substitute Specification also accompanies this Preliminary Amendment. Approval and entry of the Substitute Specification (including Abstract) is respectfully requested.

It is respectfully submitted that the subject matter of the present application is new, non-obvious and useful. Prompt consideration and allowance of the application are respectfully requested.

Respectfully submitted,
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Dated: 6/30/05

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METHOD FOR THE PRODUCTION OF A SEMI-FINISHED PRODUCT MADE OF
 ZIRCONIUM ALLOY FOR THE PRODUCTION OF A FLAT PRODUCT AND USE
 THEREOF Method For The Production Of A Semi-Finished Product Made Of
 Zirconium Alloy For The Production Of A Flat Product And Use Thereof

FIELD OF THE INVENTION

The invention ~~concerns~~ relates to a method for the production of a semi-finished product made of zirconium alloy intended for the production of a flat product used for the manufacture of fuel assembly elements.

5 BACKGROUND INFORMATION

Fuel assemblies in nuclear reactors cooled by light water, for example ~~pressurised~~ pressurized water reactors (PWR) and boiling water reactors (BWR), or fuel assemblies of CANDU reactors, contain elements comprising a zirconium alloy with the property of low neutron absorption in the heart of the nuclear reactor.

10 In the case of assemblies for PWR-type nuclear reactors, the jacket tubes for the fuel rods and the plates used for production of the spacer grids for the fuel assembly can be made of zirconium alloy, in particular zirconium alloy containing tin and iron such as the alloys Zircaloy 2 or Zircaloy 4.

15 The parallelepipedic housings of the fuel assemblies for BWR reactors are also generally produced from flat products of zirconium alloys such as Zircaloy 2 or Zircaloy 4.

20 Other alloys such as the alloy known under the commercial name M5, which essentially ~~comprising~~ comprises zirconium and niobium, are also used for the production of fuel assembly elements in the form of flat or tubular products.

25 In general the zirconium alloys used for the production of fuel assembly elements comprise at least 97% zirconium by weight, the remainder of the composition which represents at most 3% by weight, with the exception of impurities due to the production of the alloy, can comprise various elements and in particular iron, tin or niobium.

Zirconium alloys meeting these conditions in relation to their composition, depending on the temperature and the heat treatment to which they are subjected, can take one or the other of the two allotropic forms of zirconium i.e. the alpha phase, which is the phase of zirconium stable at low temperature with a compact hexagonal structure, or the beta phase, which is the phase stable at high temperature with a cubic structure.

In certain temperature ranges or at the end of certain treatments, zirconium alloys such as the technical alloys used for the production of fuel assembly elements defined above can have a mixed alpha + beta structure.

Flat products of zirconium alloy are generally produced by numerous successive stages of hot and cold forming and heat treatment.

The starting product is usually a very large ingot obtained by casting an alloy set to the required composition. Typically an ingot is cast with a diameter for example between 400 and 800 mm, and a length between 2 m and 3 m. The ingot then undergoes forging operations in a temperature range in which it can be in the α , β or $\alpha+\beta$ phase (EP-0.085.552 and US-5,674,330).

Preferably the ingot is heated so that the alloy is in the beta phase, then a first forging stage is performed on the heated ingot in the beta phase. Typically the ingot can be heated to 1050°C for ten hours before forging.

After a first forging stage, the product resulting from the forging is quenched from the beta phase.

Then a second forging stage is performed at a temperature below 800°C, the alloy being in the alpha phase, in the case of Zircaloy-type alloys. After the second forging stage, the resulting product which constitutes the semi-finished product of the process for producing a flat product, is a slab which can have a thickness of the order of 100 mm.

The slab is then subjected to various hot rolling and cold rolling operations to obtain a flat end product such as a strip with a thickness of 0.2 to 4 mm. The heat treatments of quenching and annealing are performed between at least certain of the forming operations of the flat end product.

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- The transformation process which has just been described comprises numerous phases of successive treatments and in particular several quenchings from the beta phase to obtain the semi-finished product such as a slab which is hot formed, and the second intermediate product which is cold formed.

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During the cooling stages of the products or during the quenching stages, the zirconium alloy product comes into contact with humid air and/or water so that it absorbs hydrogen which fixes in the material in the form of hydrides.

- 15 In general the presence of hydrides in the material in the form of coarse precipitates is harmful to the cold formability and corrosion resistance of the products.

Hydrides are generally precipitated in a temperature range from 220°C to 100°C during the cooling of the product, and the hydrides form in a quantity which is larger and in a form which is coarser as the material absorbs more hydrogen.

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Because it is advantageous to limit the formation of hydrides in the material or promote the preferential formation of hydrides in fine form, it is preferable to perform the transformation processes of the zirconium alloy products such that these products absorb the smallest possible quantity of hydrogen during the forming and heat treatment operations.

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It is also advantageous to be able to simplify the forming process which is complex and comprises numerous successive operations.

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French patent 2,334,763 proposes a process of heat treatment and/or thermomechanical treatment of a zirconium alloy containing over 150 ppm carbon in a temperature range between 830°C and 950°C in order to solubilise at least part of

the carbon, no subsequent heat treatment being performed at a temperature greater than 950°C.

The heat treatment or thermomechanical treatment in the temperature range of 830°C to 950°C, which corresponds to the range in which the alpha and beta phases are present in the alloy, is only performed after a first forging of an ingot in the beta phase followed by quenching in water.

The process according to French patent 2,334,763 is only suitable for zirconium alloys of a particular type and does not allow modification of the first phases of production of products during which water quenching is performed. Furthermore, production stages after the heat treatment or thermomechanical treatment in the alpha + beta phase cannot be performed at a temperature above 950°C.

The process according to the former patent is therefore limited in its applications and the results obtained in relation to the presence of hydrides in the end product.

SUMMARY

The ~~object~~ objective of the present invention is to propose a method for production of a zirconium alloy semi-finished product containing by weight at least 97% zirconium and intended for the production of flat products, in which a large ingot is produced by casting the zirconium alloy, then by forging the large ingot a semi-finished product intended to be hot rolled then cold rolled to obtain the flat product is produced, heat treatments of quenching and annealing being interspersed between at least certain of the forming operations, where this method simplifies and reduces the cost of production of the product, and limits to low levels the presence of hydrides which have a harmful effect on the formability and corrosion resistance of the zirconium alloy product.

To this end the semi-finished product is produced from the large cast ingot by a single forging operation at a temperature at which the zirconium alloy is in a state comprising the crystalline α and β phases of the zirconium alloy.

According to particular features:

- at the forging temperature, the ingot comprises a volume proportion of zirconium alloy in the α phase between 10% and 90%, the rest of the zirconium alloy of the ingot being in the β phase,
- the semi-finished product is a slab;
- 5 – the slab has a thickness of around 100 mm and is intended for production of a flat product having a thickness between 0.2 mm and 4 mm;
- the forging of the zirconium alloy in the α and β phase is performed at a temperature between 850°C and 950°C; and
- the zirconium alloy comprises at least 3% by weight in total of additional elements
- 10 comprising at least one of the elements tin, iron, chromium, nickel, oxygen, niobium, vanadium and silicon, the remainder of the alloy being constituted by zirconium with the exception of the inevitable impurities.

The invention also relates to the use of the method for production of a slab intended
15 for production of a flat product of a thickness between 0.2 mm and 4 mm for the manufacture of a nuclear fuel assembly element such as a plate of a spacer grid for the fuel assembly of a PWR reactor or a wall of a fuel assembly housing for a BWR reactor or again a fuel assembly element for a CANDU reactor.

20 In order to understand the invention, in a comparison a production method will be described for a semi-finished product intended for production of flat products according to the prior art and according to the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a diagram showing in a symbolic manner the various stages of the
25 production method of the prior art.

Figure 2 is a diagrammatic representation similar to that in figure 1 of the production method according to the invention serving to produce the semi-finished product.

30 DETAILED DESCRIPTION

Figure 1 shows a cast ingot 1 which can be a large ingot, the diameter of which can

be between 400 mm and 800 mm and the length between 2 m and 3 m, which is obtained by casting a zirconium alloy used for the production of flat products for the manufacture of fuel assembly elements.

- 5 The zirconium alloy can be for example a Zircaloy 2 alloy comprising in weight from 1.2% to 1.7% tin, 0.07% to 0.20% iron, 0.05% to 0.15% chromium, 0.03% to 0.08% nickel, at most 120 ppm silicon and 150 ppm carbon, the remainder of the alloy being constituted by zirconium with the exception of the usual impurities.
- 10 The alloy for production of the flat product can be also a Zircaloy 4 comprising by weight 1.2% to 1.7% tin, 0.18% to 0.24% iron, 0.07% to 0.13% chromium, at most 150 ppm carbon, the remainder of the alloy being constituted by zirconium and impurities.
- 15 The alloy is cast as a large ingot 1 which is then brought to a temperature higher than 1000°C and for example a temperature of 1050°C for ten hours so that the alloy of the ingot is entirely in the beta cubic phase, stable at high temperature.

The cast ingot is then forged at a temperature in the beta range of the alloy and for example at a temperature close to 1000°C in the form of a flat product of substantial thickness known as a slab, as shown by stage 2 on figure 1.

The thick slab 3 then undergoes quenching in water or humid air as shown symbolically by the arrows representing a third stage 4 of the production process.

25 In a fourth stage indicated by 5 in figure 1, the thick slab 3 is forged at a temperature in the alpha range of the zirconium alloy, for example at a temperature of the order of 800°C.

30 This gives a slab 3 with a thickness of the order of 100 mm which constitutes the semi-finished product from the forging and undergoes hot rolling then cold rolling to obtain the flat end product in the form of a sheet or strip of a thickness which can be between 0.2 mm and 4 mm.

The initial forging of the ingot 1 in the beta phase (stage 2 of the process) must be followed by quenching in the beta phase (stage 2 of the process) as the metal, which cools during forging, can contain an external zone in the alpha+beta phase leading to the formation of segregations of alphagenic elements such as tin and oxygen and betagenic elements such as iron, chromium, nickel or niobium, depending on the elements contained in the alloy.

These segregations are harmful to the properties of use of the alloy and in particular the properties of corrosion resistance and suitability for deep drawing.

Quenching in the beta phase entails the slab 3 coming into contact with a quenching environment constituted by water or humid air, i.e. an environment containing hydrogen.

Hydrogen is absorbed by the slab at the time of heat treatment and fixes inside the alloy in the form of hydrides.

The forming suitability and corrosion resistance of the flat product of zinc alloy consequently deteriorate.

The method according to the invention for the production of a slab intended for the production of flat products will be described in relation to figure 2.

The large cast ingot 1 of zirconium alloy is subjected to a single forging operation 7 in the $\alpha+\beta$ phase to obtain the slab 8 substantially similar to the slab 3 obtained by the complex forging process in the β phase, quenching from the β phase and forging in the α phase.

The method according to the invention thus comprises replacing the three first stages 2, 4 and 5 of the process of the prior art, i.e. stage 2 of forging in the beta phase (above 1000°C) followed by stage 4 of quenching the slab 3' from the beta phase and forging in the alpha phase at a temperature below 800°C, with a single

stage 7 of forging in the $\alpha+\beta$ phase, for example in the case of alloys Zircaloy 2 and 4, at a temperature between 850°C and 950°C and for example at a temperature of the order of 900°C.

- 5 The temperature for the $\alpha+\beta$ phase forging is selected so that the volume proportion of the α phase in the ingot alloy is between 10% and 90%, the remainder of the alloy being in the β phase.

10 The ingot 1 is forged to give a slab 8 of thickness which can be of the order of 100 mm and which constitutes the semi-finished product that will then be subjected to the operations of hot rolling and cold rolling as described above, separated by stages of quenching and annealing as heat treatment.

15 By performing analyses on the semi-finished product 8 or on the flat products obtained from the semi-finished product, it can be observed that the quantity of hydrides contained in the alloy obtained by the process according to the invention is substantially smaller than the quantity of hydrides contained in a product according to the prior art.

20 On the semi-finished product which is a slab in the case of production of flat products, a hydrogen content has been measured which is twice as low as in the process of the prior art, when forging in the $\alpha+\beta$ phase is used instead of the three initial stages of the production process according to the prior art.

25 The hydrides precipitated in the product according to the invention are also of a size generally smaller than the hydrides precipitated in a flat product according to the prior art.

30 The properties of corrosion resistance and formability of the flat product made from the semi-finished product obtained according to the invention are therefore markedly superior to those of a product obtained in the process according to the ~~prior art~~ conventional processes.

These advantageous and surprising results may be due to the absence of high temperature quenching on a slab obtained by forging in the β phase.

- 5 In fact this high temperature quenching on the slab 3' which is achieved with a quenching medium containing hydrogen produces an absorption of hydrogen by the product and the subsequent formation of hydrides.

Also one of the advantages of the method according to the invention is to simplify considerably the process of production of the semi-finished product. This therefore leads to a substantial reduction in cost and duration in the implementation of the process.

Also the product is only brought to a temperature in the α and β range, i.e. a temperature markedly lower than the sustained temperature in the β phase of the process in the prior art.

In the case of the Zircaloy 2 and Zircaloy 4 alloys of which the composition is given above, the forging of the ingot 1 in the $\alpha+\beta$ phase is performed in a temperature interval ranging from 850°C to 950°C and for example at 900°C.

In the case of the Zircaloy 2 and Zircaloy 4 alloys or any other alloy containing tin, the transition to the $\alpha+\beta$ phase of the alloy, to perform the forging of the method according to the invention, can lead to the formation of tin segregations.

However, these segregations can be suppressed by subsequent processing within the context of production of the flat end product from the semi-finished product.

In the case where the process of the invention is applied to niobium alloys, in which the transition between the α and $\alpha+\beta$ phases is close to 600°C, the forging temperature in the $\alpha+\beta$ phase can be substantially lower than 900°C taking into account however the malleability properties of the alloy at the forging temperature.

Application of the process according to the invention to zirconium alloys other than Zircaloy or to niobium alloys can be considered. These alloys generally contain at most 3% in weight of additive elements comprising at least one of the additive elements tin, iron, chromium, nickel, oxygen, niobium, vanadium and silicon, the remainder of the alloy being constituted by zirconium and the inevitable impurities.

The invention applies in particular to the production of a flat product of zirconium alloy for the manufacture of fuel assembly elements such as plates for the manufacture of spacer grids for assemblies for PWR-type nuclear reactors or housing walls for assemblies for BWR reactors or for fuel assembly elements for CANDU reactors.

The invention is not limited strictly to the embodiments described.

The temperature for forging in the $\alpha+\beta$ phase depends on the composition of the zirconium alloy. The forging operations can be performed using the normal means for forging in the α phase or β phase of the process of the prior art or other means adapted to $\alpha+\beta$ phase forging in a single operation to obtain a slab.

The invention applies generally to any technical zirconium alloy product defined by the composition limits given above.

COMPAGNIE EUROPEENNE DU ZIRCONIUM-CEZUS

**Method for the Production of a Semi-Finished Product made of Zirconium Alloy
for the Production of a Flat Product and Use Thereof**

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ABSTRACT OF THE TECHNICAL CONTENT OF THE INVENTION

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A large ingot (4) is produced by casting the zirconium alloy, then the ingot is forged to obtain the semi-finished product (8) wherein .The the semi-finished product (8) which can be a slab for production of a flat product is produced from the large cast ingot (4) in a single forging operation (7) at a temperature at which the zirconium alloy is in a state comprising both the crystalline α and β phases of the alloy.

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Figure 2.